

DISSOCIATION CONSTANTS OF SUBSTITUTED BENZOIC ACIDS IN ANHYDROUS DIMETHYL SULPHOXIDE

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Dissociation constants of twenty-one 3- and 4-monosubstituted and seven 3,4-disubstituted benzoic acids have been measured in anhydrous dimethyl sulphoxide. The constants measured correlated with the Hammett σ constants ($\rho = -2.43$); the Exner coefficient λ 1.135 has been found.

In a number of papers¹⁻³ we dealt with the influence of polysubstitution on a reaction centre by using predominantly kinetic measurements. We decided to turn our attention to the influence of more substituents on acid-base equilibria, too. In our first paper⁴ we studied the dissociation constants of disubstituted benzoic acids in water, 50% aqueous ethanol, and 80% aqueous methyl cellosolve. We have chosen anhydrous dimethyl sulphoxide as a medium for our further study, which guarantees sufficient solubility and a relatively simpler interpretation of the influence of medium on the dissociation constants as compared to that of mixed solvents. Besides that it can be anticipated that the reaction centre will be fundamentally more sensitive towards the substituent polar effects than in other solvents. *E.g.* the ρ constant of dissociation of benzoic acids is 1.37 and 1.64 in 50% ethanol and 80% methyl cellosolve, respectively, the estimate⁵ and extrapolation⁶ for dimethyl sulphoxide being 2.6 and 2.47, respectively. With respect to the fact that Kolthoff and Chantooni⁷ published the dissociation constants of some benzoic acids in this solvent, we have decided to publish the results obtained by us so far.

EXPERIMENTAL

The substituted benzoic acids used were described in a previous report⁸. Anhydrous dimethyl sulphoxide was obtained by shaking the commercial product with calcium oxide, pouring through Nalsit and vacuum distillation (b.p. 56°C/5 Torr). It was kept in dark bottles over Nalsit under nitrogen. The titration reagent — about 2M-tetrabutylammonium methoxide in anhydrous methanol — was prepared from tetrabutylammonium iodide on a ionex column packed with Anex — S 8 TM resin. This stock solution was kept under nitrogen in refrigerator. Fresh titration solution was prepared therefrom every day by diluting with dimethyl sulphoxide down to a concentration about 0.1M. The dissociation constants were determined potentiometrically. The electro-

motive force of a cell: glass electrode/HA (dimethyl sulphoxide) AgNO_3 (0.1N in dimethyl sulphoxide), Ag was measured on a millivolt scale of a pH-meter PHM-4d (Radiometer, Copenhagen). The glass electrode G2000B (Radiometer, Copenhagen) was used as indicator electrode, and its function was checked in a series of aqueous buffers: the change 59.2 mV/pH was found over the whole range studied. The titration of about $3 \cdot 10^{-3}$ M solutions of each acid was carried out in a thermostated vessel ($25.0 \pm 0.1^\circ\text{C}$) under the nitrogen free of moisture and carbon

TABLE I

Dissociation Constants of Substituted Benzoic Acids in Dimethyl Sulphoxide at 25°C

No	Benzoic acid	M.p., $^\circ\text{C}$	pK	
			found	literature
1	<i>p</i> -Amino-	187–188	12.48	—
2	<i>p</i> -Hydroxy-	214–215	11.72	—
3	<i>m</i> -Amino-	169–172	11.43	11.6 ^{a,b}
4	<i>p</i> -Methyl-	179–180	11.42	—
5	<i>m</i> -Methyl-	110–111	11.26	11.0 ^a
6	Unsubstituted	122	11.02	11.0 ^{a,c}
7	<i>m</i> -Hydroxy-	203	11.19	11.1 ^a
8	<i>p</i> -Chloro-	242–243	10.36	10.1 ^a
9	<i>p</i> -Bromo-	252–253	10.6	10.5 ^d
10	<i>p</i> -Carboxymethyl-	220–221	10.15	—
11	<i>m</i> -Acetyl-	172	10.22	—
12	<i>m</i> -Carboxymethyl-	192–194	10.1	—
13	<i>m</i> -Bromo-	154–155	9.91	9.68 ^e
14	<i>m</i> -Chloro-	158	9.82	—
15	<i>p</i> -Acetyl-	200–205	9.77	—
16	<i>m</i> -Sulfamido-	242–243	9.81	—
17	<i>p</i> -Sulfamido-	289–290	9.71	—
18	<i>m</i> -Cyano-	217	9.44	—
19	<i>p</i> -Cyano-	219–220	9.27	—
20	<i>m</i> -Nitro-	140–141	9.20	9.2 ^{d,f}
21	<i>p</i> -Nitro	238–240	9.07	9.00 ^{d,g}
22	3,5-Dinitro-	204–205	7.61	7.4 ^h
23	3-Iodo-4-amino-	201–202	11.6	—
24	3-Bromo-4-hydroxy-	158	11.0	—
25	3-Nitro-4-chloro-	—	—	8.62 ⁱ
26	3-Nitro-4-bromo-	203–204	8.86	—
27	3-Nitro-4-iodo-	213	8.65	—
28	3-Bromo-4-methylsulfonyl-	202–203	8.26	—
29	3-Iodo-4-methylsulfonyl-	208–210	8.66	—

^a Ref. ⁵; ^b ref. ¹¹ and ¹² give pK 11.4 and 11.0 respectively; ^c the same value is given in ref. ^{7,11,13}, ref. ¹² gives 10.9; ^d ref. ¹¹; ^e ref. ¹³; ^f ref. ⁷ gives 9.17; ^g ref. ⁵ gives 8.9, ref. ⁷ gives 9.04; ^h ref. ¹², ref. ⁷ gives 7.40. ⁱ ref. ⁷

dioxide and saturated with dimethyl sulphoxide vapours. The apparatus was calibrated by titration of benzoic and 3,5-dinitrobenzoic acids (pK_a 11.0 and 7.6 respectively⁹). These values were used for determination of the pH scale.

RESULTS AND DISCUSSION

The dissociation constants of twenty-one mono- and seven disubstituted benzoic acids measured are listed in Table I. By plotting the pK measured against the Hammett σ constants¹⁰ a linear relation was obtained ($\rho = -2.43$, s 0.05, r 0.995, n 26). The high ρ value in this solvent at 25°C indicates that the reaction centre is considerably sensitive towards polar effects of substituents. Our value agrees with that of Kolthoff (2.4, ref.⁷) and with the prediction of Hojo (2.47, ref.⁶). On the contrary, Ritchie⁵ gives a higher value (2.6). From the results summarized in Table I it follows that the normal σ constants can be used for dissociation of *m*- and *p*-substituted benzoic acids even in the medium of a dipolar aprotic solvent as *e.g.* dimethyl sulphoxide. From the set of acids measured a statistically significant deviation is encountered only with *m*-hydroxybenzoic acid. The value found is higher than that calculated from the respective σ constant (0.09) by 0.42 pK units. A correlation according to equation¹⁰ $pK_p - pK_o = \lambda(pK_m - pK_o)$ was carried out for selected acids having electron-attracting substituents ($COCH_3$, CO_2CH_3 , SO_2CH_3 , CN and NO_2). The coefficient λ in anhydrous dimethyl sulphoxide has a value 1.135 which agrees with that calculated by Exner¹⁰ (1.14) for mixed solvents (50% by vol. ethanol and 80% by wt. methyl cellosolve).

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